

# Quasicrystalline valence bands in decagonal AlNiCo

Eli Rotenberg,\* W. Theis,<sup>†</sup> K. Horn,<sup>‡</sup> and P. Gille<sup>§</sup>

\*MS2-400, Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

<sup>†</sup>Fachbereich Physik der Freien Universität Berlin, Germany

<sup>‡</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

<sup>§</sup>Institut für Kristallographie und Angewandte Mineralogie der Ludwig-Maximilians-Universität München, Germany

Quasicrystals possess perfect long-range structural order in spite of the fact that their rotational symmetries are incompatible with long-range periodicity. The exotic structural properties of this class of materials, discovered by Shechtman *et al.*<sup>1</sup> in 1984, are accompanied by physical properties that are unexpected for metallic alloys. While considerable progress in resolving the geometric structures of quasicrystals has been made through x-ray and neutron diffraction and new theoretical concepts such as the quasi-unit-cell model,<sup>2</sup> the basic properties of the valence electronic states, i.e. whether they are extended as in periodic crystals or localized as in amorphous materials are still largely unresolved.<sup>3</sup> An investigation of the “mysterious electronic bandstructure of quasicrystals”<sup>3</sup> is therefore timely and important. Here we show, through angle-resolved photoemission experiments from decagonal Al<sub>71.8</sub>Ni<sub>14.8</sub>Co<sub>13.4</sub>, that the *s-p* and *d* states exhibit band-like behavior with the symmetry of the quasiperiodic lattice. We find that the Fermi level  $E_F$  is crossed by dispersing *d*-bands.

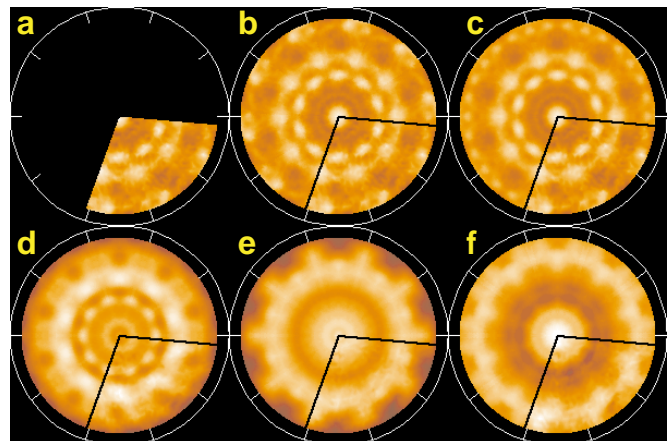
As a consequence of their translational symmetry, ordinary periodic crystals have electronic bands comprised of wavefunctions in the Bloch form,  $\Psi_{\mathbf{k}} = u_{\mathbf{k}}(r)e^{i\mathbf{k}\cdot\mathbf{r}}$ , where the plane wave with wavevector  $\mathbf{k}$  is modulated by the lattice-periodic function  $u_{\mathbf{k}}(r)$ . (With the convention that  $\hbar=1$ , electron wavevector  $\mathbf{k}$  and crystal momentum  $\mathbf{p}=\hbar\mathbf{k}$  are equivalent). A further consequence is that the reciprocal  $\mathbf{k}$ -space ordering is also periodic, with the bandstructure from the central Brillouin zone repeated in each primitive unit cell in  $\mathbf{k}$ -space. In random systems, on the other hand, the translational symmetry is lost,  $\mathbf{k}$  is no longer a good quantum number, and disorder leads to the formation of localized eigenstates with an exponential decay of the amplitudes<sup>4</sup>. A fundamental, open question is whether valence states in quasicrystals exhibit band-like behavior, with the concepts of crystal momentum and Brillouin zones adapted to aperiodic order,<sup>5,6</sup> or else exhibit localized or “confined” states<sup>7</sup> which one might expect in view of the cluster-like structure of quasicrystals.

The electronic structure of quasicrystals has been intensely studied by means of electrical resistivity, magnetoresistivity, Hall effect, and thermopower experiments,<sup>8</sup> among others, and important information is gained from these measurements. The interpretation of such experiments in terms of the character of the electronic states is not straightforward, however. Angle-resolved photoemission, on the other hand, yields direct information on the nature and  $\mathbf{k}$ -dependent dispersion of electronic states,<sup>9</sup> hence this method is ideally suited in our quest for the band-like character of quasicrystalline electronic states. An earlier report in fact found some evidence for such states in icosahedral AlPdMn.<sup>10</sup> In contrast, we chose Al<sub>71.8</sub>Ni<sub>14.8</sub>Co<sub>13.4</sub> decagonal quasicrystals (henceforth AlNiCo) for our study since they possess both regular crystalline order (along the tenfold axis) and quasiperiodic order (normal to the

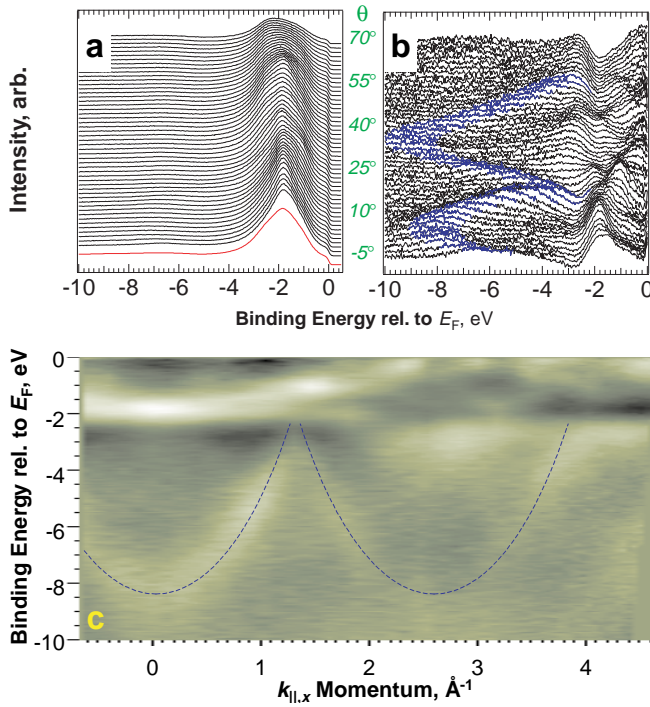
tenfold axis), offering the fascinating opportunity to observe quasicrystalline and crystalline ordering in the same bands, by examining the  $\mathbf{k}$ -space distribution of electrons moving within and out of the surface plane. AlNiCo crystals were grown by the Czochralski method,<sup>11</sup> and samples with tenfold surfaces were cut and polished following orientation by Laue x-ray diffraction. The surface was cleaned by ion bombardment followed by annealing in the ultra-high vacuum chamber and was characterized by low energy electron diffraction (LEED), secondary electron imaging,<sup>12</sup> and core-level photoelectron diffraction, all of which demonstrated a tenfold symmetric pattern characteristic of quasicrystalline order. Surface preparation and experiments were performed at beamline 7.0 at the Advanced Light Source, with a combined instrumental energy resolution of  $\sim 55$  meV and an angular acceptance better than 1.4 degrees. Angle-resolved valence bands were recorded by rotating the sample polar ( $\theta$ ) and azimuthal ( $\phi$ ) angles with the analyzer and light source orientations fixed.<sup>13</sup> By measuring the kinetic energy and angles of emission relative to the sample surface, one can with simple assumptions determine the three-dimensional momenta  $\mathbf{k}$  of the electrons.<sup>9</sup>

That the valence electrons “feel” the symmetry of the quasicrystalline structure can be readily inferred from a set of angular intensity maps of the valence electrons, representing the photoemission intensity emitted into a partial angular sector above the sample (Fig. 1a). The repeating elements in this image are separated by  $36^\circ$  azimuth angle, providing clear evidence of a tenfold rotationally symmetric emission pattern. Experimental noise can therefore be reduced by a tenfold rotational averaging of the data (Fig. 1b). Because of the arbitrary orientation of the light’s polarization vector to our sample surface, the photoemission data show a slight breaking of mirror-plane symmetry that changes the intensities (but not positions) of features across mirror planes. We can restore the intrinsic mirror-plane symmetry, demonstrated by electron diffraction data (Fig. 3a), by a further mirror averaging (Fig. 1c).

The data show a complex pattern with many strong and subtle features. The least-bound electrons at the Fermi energy ( $E_F$ ) (Fig. 1a-c) display various sharp maxima at specific emission angles which appear to evolve continuously as deeper energies are sampled (Fig. 1d-f). The evolution of these patterns, occurring



**Figure 1.** Angle-resolved photoemission intensity maps for AlNiCo valence band electrons for various binding energies relative to the Fermi level  $E_F$ , acquired for photon energy 130 eV. (a) raw data for electrons at  $E_F$  emitted into a  $105^\circ$  azimuth range. The radial coordinate is proportional to the polar angle of emission  $\theta$  from  $0^\circ$  (center) to  $42^\circ$  (outer rim). (b,c) the same data as in (a) is compared to tenfold rotational and mirror-plane averaging, resp. (d-f) similarly processed data for electron energies 1.03, 1.84, 2.77 eV below  $E_F$ , respectively.



**Figure 2.** Angle-resolved photoemission spectra for AlNiCo valence electrons for photon energy 95 eV. (a) a series of photoemission spectra for various polar angles  $\theta$ . The bold, red spectrum at the bottom is the angle-integrated spectrum. (b) the same data upon normalizing to the angle-integrated spectrum. The states indicated in blue, weak in (a), are now apparent. (c) an intensity plot of the same data, now in the form of a conventional bandmap, obtained after mapping the angle  $\theta$  into momentum  $k_{||,x}$ . The dashed line indicates the parabolic band-like character of the  $s$ - $p$ -derived states.

rapidly over just a few electron volts, suggests that the electronic states disperse continuously with momentum  $\mathbf{k}$ . Such rapid changes over a narrow energy range rule out an explanation of these patterns in terms of elastic scattering of the electrons after the photoemission event.<sup>14</sup>

To prove that the electronic energies disperse continuously with  $\mathbf{k}$ , we acquired valence band spectra vs. momentum parallel ( $\mathbf{k}_{||}$ ) to the tenfold symmetric sample surface. Fig. 2a shows a set of spectra recorded at different polar emission angles  $\theta$  along  $k_{||,x}$ , one of the twofold axes in the  $\mathbf{k}_{||}$ -plane. The spectra are dominated by a broad peak at around 2 eV binding energy, due mostly to the Co and Ni  $d$ -electrons, but additional, weaker contributions from Al, Ni, and Co  $s$ - $p$  electrons are also present down to about 8.5 eV below  $E_F$ . (The  $s$ - $p$  states appear weak merely as a consequence of their low relative photoemission cross sections.) Deviations from the angle-averaged spectrum (red line) clearly demonstrate a  $\mathbf{k}$ -dependence of the  $d$ -derived spectral features.

In order to raise the  $s$ - $p$  states to the same scale as the  $d$ -states, we have divided the angle-resolved spectra by the angle-averaged spectrum and plotted the resulting normalized data as individual spectra in Fig. 2b and as an intensity map in Fig. 2c. The normalized data in Figs 2b-c reveal two new bands, assigned to  $s$ - $p$ -derived states, which strongly disperse from 3 to 8.5 eV binding energy; they have an almost free electron-like dispersion--their energy follows the simple parabolic form  $E = \hbar^2 k^2 / 2m^*$ , with an effective mass  $m^*$  of about 0.9 electron masses. The changes in the  $d$ -level region are difficult to assign, but we can identify at least one band-like feature, with its highest binding energy at normal emission ( $\theta=0^\circ$ ,  $\mathbf{k}_{||}=0$ ), that turns upwards and appears to cross  $E_F$  at about  $k_{||}=2.5 \text{ \AA}^{-1}$ . The complete map of such crossings, of which Fig. 1c is just a partial sampling, forms the Fermi surface, whose

topology is important for predictions of anomalous transport properties<sup>15</sup> and may also contribute to the stability of quasicrystals.

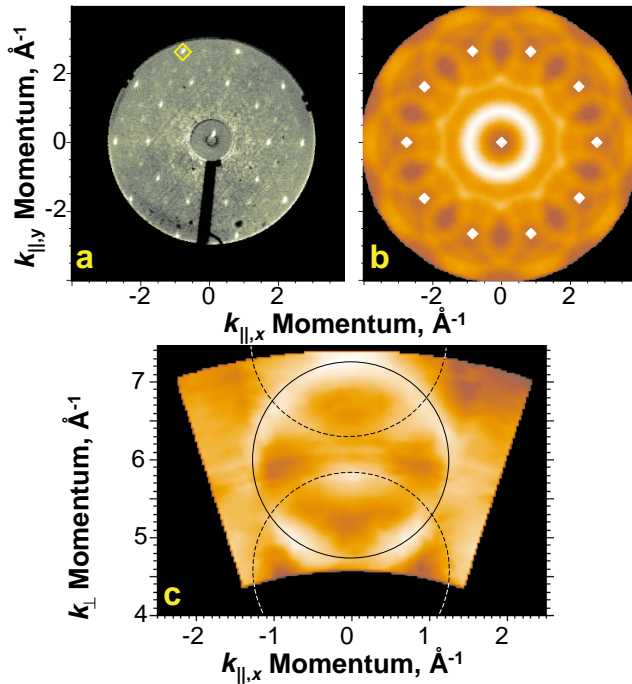
We can exploit the simple parabolic dispersion of the  $s$ - $p$  states to observe the quasiperiodic ordering of the bands in  $\mathbf{k}$ -space. In Fig. 3a, we show a tenfold symmetric LEED diffraction pattern from our sample for an electron kinetic energy of 71.5 eV. The LEED pattern emerges from scattering at the atomic cores and therefore derives from the aperiodic geometry. The diffraction pattern from a quasicrystalline surface in principle forms a set that is dense in  $\mathbf{k}$ -space, i.e. there is an unlimited number of “reciprocal lattice vectors” and thus an unlimited number of diffraction spots.<sup>16</sup> However, as is obvious from the pattern in Fig. 3, there is a set of spots with dominant intensities that may be taken to construct a “quasi-Brillouin zone” if we consider only the dominant Fourier components of the lattice potential.<sup>5,6</sup> Similar to the case of periodic crystals, we may expect to observe bands from the center of the quasi-Brillouin zone to be replicated to the positions of the principal (and possibly weaker) diffraction spots.

To test this idea, we have sampled the four experimental degrees of freedom (binding energy  $E$ , in-plane momentum  $\mathbf{k}_{||}=(k_{||,x}, k_{||,y})$  and out-of-plane momentum  $k_{\perp}$ ) in another way. Since the free-electron energy is  $E = \hbar^2 k^2 / 2m^*$ , then for constant energy the electron momenta are restricted to spherical surfaces in 3-dimensional  $\mathbf{k}$ -space. Circular, cross-sectional cuts through these spheres can be visualized by sampling the  $\mathbf{k}$ -dependent intensity distribution of electrons (with energy 6 eV below  $E_F$ ) in two complementary ways. In Fig. 3b, we show data for electrons at constant  $|\mathbf{k}|$ , sampling states over a wide range of  $\mathbf{k}_{||}$ . In Fig. 3c we show states in the  $k_{||,x}$ - $k_{\perp}$ -plane, thus sampling over a wide range of  $k_{\perp}$  near  $\mathbf{k}_{||}=0$ .

In Fig. 3b, we observe a circular ring around the center ( $\mathbf{k}_{||}=0$ ) and ten outlying rings of equal diameter. The central and the ten outer rings correspond to 6 eV level crossings of the bands from Fig. 2c centered at  $k_{||,x}=0$  and  $\sim 2.5 \text{ \AA}^{-1}$ , respectively. Furthermore, we find that the ten outer rings are centered on each of the dominant diffraction spots in Fig. 3a. Therefore, the  $s$ - $p$  band emerging from the central quasi-Brillouin zone has its counterparts in identical bands distributed aperiodically in  $\mathbf{k}$ -space. Their arrangement is easily understood in terms of a repeated zone scheme due to the influence of the in-plane aperiodic potential.

Since there is a periodic arrangement of atomic planes normal to the sample surface, we expect a periodic repetition of bands in this direction. This is readily observed in the data in the  $k_{||,x}$ - $k_{\perp}$ -plane, Fig. 3c. Ring-like contours are again observed, corresponding to the  $\mathbf{k}$ -space unit cells along the tenfold axis; however, in contrast to the quasiperiodic ordering of the bands with its tenfold symmetry forbidden in periodic crystals, the ring-like features here are arranged equidistantly. This arrangement continues for at least 4 complete periods along  $k_{\perp}$  for both the  $s$ - $p$  and the  $d$ -bands. The distance between rings,  $1.55 \text{ \AA}^{-1}$ , corresponds to an interlayer distance of  $d = 2\pi/1.55 \text{ \AA}^{-1} = 4.05 \text{ \AA}$ , in good agreement with x-ray diffraction measurements ( $4.08 \text{ \AA}$ ).<sup>17</sup> This demonstrates that periodic ordering prevails in the direction parallel to the tenfold axis as expected from the structure of AlNiCo.

How do the electronic wavefunctions in a quasicrystal compare to those in a periodic metal? The diffraction pattern consists of a few dominant spots, suggesting that the atomic distribution (and hence the electrostatic potential entering the Schrodinger equation) can be expanded in terms of an aperiodic lattice in  $\mathbf{k}$ -space. The solutions to the Schrodinger equation will therefore be of the form  $\Psi_{\mathbf{k}} = u_{\mathbf{k}}(r)e^{i\mathbf{k}\cdot\mathbf{r}}$ , which is similar to the Bloch form for conventional crystals. The main difference between



**Figure 3.** In-plane and out-of-plane order in  $k$ -space. (a) Low-energy electron diffraction pattern for 71.5 eV electrons, showing the tenfold, in-plane aperiodic order. (b) Emission profile of 6 eV binding energy electrons, for a wide range of in-plane electron momenta  $k_{\parallel}$ . A central and ten outer rings are observed, establishing that the  $s$ - $p$  electrons sample the aperiodic order. The brightest, outermost ring of spots in (a) are reproduced in (b) by the diamonds. (c) A vertical cut through the central spherical constant-energy surface shows a strong central ring (solid) with somewhat weaker circles spaced equally above and below it (dashed).

quasicrystals and periodic crystals is that in the latter  $u_{\mathbf{k}}(r)$  is a Fourier series over the periodic reciprocal lattice and therefore has the full real-space periodicity of the solid, while in the present case  $u_{\mathbf{k}}(r)$  is a summation over the countably dense, aperiodic reciprocal lattice. This appears to be a useful expansion<sup>3</sup> since only a few special reciprocal lattice points dominate the spectra, consistent with our observation of parabolic bands centered on the same reciprocal lattice points as the principal electron diffraction spots.<sup>5,6</sup>

The photoemission data are important for characterizing the electronic states of quasicrystals. The eigenvalue spectrum of a system can be classified as continuous or discrete, corresponding to extended or localized eigenstates. Continuous spectra are characteristic for periodic systems, where Bloch's theorem holds, but in random systems such as amorphous metals, a discrete spectrum occurs, and the states are localized with an exponential decay of the amplitudes.<sup>4</sup> Our work is significant because it shows that the localization of states in  $k$ -space appears sufficient to ensure that at least some states are extended in real space (although the possibility remains that there are additional localized states present). Furthermore, the wide band widths (2-8 eV) and small effective masses (comparable to free electrons) indicate a high degree of extended character both within and out of the quasicrystalline planes.

In fact, quasicrystals may be an intermediate case, as shown by renormalization group studies of 1D quasiperiodic chains, in that they have critical states characterized by a power law decay of their amplitudes.<sup>18</sup> These states are derived from states localized to a cluster of size  $d$  which can resonantly tunnel to identical nearby clusters. These neighboring clusters are separated by a distance  $2d$  or less apart according to Conway's theorem,<sup>19</sup> which is apparently

satisfied for AlNiCo.<sup>2</sup> Critical eigenstates in quasicrystals thus derive their properties from both limiting cases, i.e. a dispersion relation according to the potential distribution of the local environment, but with amplitudes that are strongly dampened. Our data cannot rule out the possibility that the eigenstates are critical; in fact the dampening of such states may explain the weakness of features in our spectra--both  $s$ - $p$ - and  $d$ -derived--when compared to band-like emission from periodic crystals.

In summary, we have obtained clear evidence for band-like behaviour of the valence electronic states in quasicrystals, with free-electron-like bands from the  $s$ - $p$  region of the spectrum, and  $d$ -bands that disperse towards  $E_F$  in a manner suggesting a Fermi level crossing. The distribution of these states in momentum space is clearly correlated with the diffraction pattern of the surface and strongly supports the notion that the states are not dominated by localization.

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